



# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Addition Products of Substituted Phenols and Glycidol

We, OLIN MATHIESON CHEMICAL CORPORATION, a Corporation organized and existing under the laws of the State of Virginia, United States of America, of 460 Park Avenue, New York 22, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns non-ionic surfactants. Surfactants according to the invention have been found to be soluble in and readily compatible with concentrated aqueous solutions of inorganic salts, especially sodium salts.

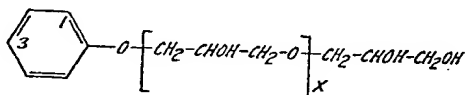
It is generally known that non-ionic surfactants based upon ethylene oxide are not compatible with concentrated aqueous solutions of most inorganic salts, but separate out as oily aqueous layers. Consequently, it is necessary in the soap and detergent industry to introduce coupling agents known as "hydratropes" into such mixtures in order to eliminate or lessen the separation of phases. Such hydratropes are, for example, sulfonated xylenes and sulfonated toluene.

It is necessary to use high proportions of alkaline builders in conjunction with surfactants in the preparation of liquid, heavy duty detergents in order to accomplish effective soil removal. However, the incorporation of soda ash and sodium tripolyphosphate into ethylene oxide-based non-ionic detergent solutions is often not practicable at high concentrations even with hydratropes, since phase separations may occur on storage due to temperature changes. In order to minimize this, the industry has had to use the more soluble potassium salts, notably, potassium carbonate and potassium phosphates, which, however, are more expensive than the sodium salts, and are consequently an economic burden.

Finally, it is also generally known that surfactants are precipitated by concentrated brine solutions, notably, saturated aqueous sodium chloride; and, consequently, it is difficult to effectively utilize surfactants in strong brine solutions which are often encountered in the secondary recovery of oil from oil bearing sands and clays.

According to the invention, there is provided a process for preparing a water-soluble adduct of glycidol and an alkylphenol, said adduct having the formula

(I)

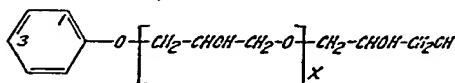


in which one of the numbered positions in the benzene ring is occupied by an alkyl group having 8 to 18 carbon atoms, and the other numbered position is occupied by hydrogen or an alkyl group having 1 to 18 carbon atoms, wherein x has a value of at least 4.5, and wherein the ratio of the value of x to the total number of carbon atoms in the alkyl groups at positions No. 1 and No. 3 is at least 0.50, which process comprises adding glycidol to an alkylphenol heated to a temperature in the range between 100 and 200°C. at a rate sufficient to maintain the glycidol concentration in the result-

ing reaction mass below about 2% by weight for a sufficient time to yield a product in which x in the above formula is above at least 4.5.

There is also provided, according to the invention a water-soluble adduct of glycidol and an alkylphenol, said adduct having the formula

(I)

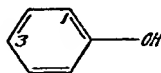


in which one of the numbered positions in the benzene ring is occupied by an alkyl group having 8 to 18 carbon atoms, and the other numbered position is occupied by hydrogen or an alkyl group having 1 to 18 carbon atoms; wherein x has a value of at least 4.5, and wherein the ratio of the value of x to the total number of carbon atoms in the alkyl groups at positions No. 1 and No. 3 is at least 0.50.

Compounds according to the invention have been found to possess the property of being readily soluble in and compatible with saturated brine solutions (NaCl), or other alkali metal chlorides, or with concentrated aqueous solutions of hydroxides, carbonates, phosphates, and silicates of alkali metals such as sodium and potassium. The compounds have cloud points above 100°C., i.e. they do not come out of aqueous solutions at 100°C. They thus possess outstanding and useful properties, as disclosed herein, which makes them particularly valuable in the surfactant industries.

The compounds according to the invention are obtained by heating glycidol with an alkylphenol having the formula

(II)



wherein one of the numbered positions in the benzene ring is occupied by an alkyl group having 8 to 18 carbon atoms, and the other numbered position is occupied by a substituent selected from the group consisting of hydrogen and an alkyl group having 1 to 18 carbon atoms.

Typical illustrative examples of suitable alkylphenols which can be employed in the preparation of the novel compounds of this invention include:

p-isononylphenol  
p-isododecylphenol  
o-, p-di-isononylphenol  
o-, p-di-isododecylphenol  
p-tertiary-octylphenol  
o-p-di-tert-octylphenol  
p-tert-octyl-o-isononylphenol  
p-tert-octyl-o-isododecylphenol  
p-sec-octylphenol  
p-sec-dodecylphenol  
p-sec-hexadecylphenol  
p-sec-octadecylphenol  
o-p-di-dodecylphenol  
p-cetylphenol  
p-octadecyl-o-cresol  
p-tertiary-octyl-o-ter-butylphenol  
p-iso-nonyl-o-tert-butylphenol

and mixtures thereof.

There is theoretically no upper limit to the number of moles of glycidol that can be used per mole of the alkyl-phenol, for the purpose of this invention. For practical purposes, approximately 30 moles of glycidol per mole of alkylphenol can be considered a practical upper limit; especially if highly alkylated phenols such as o-p-di-iso-octadecylphenol, o-p-di-iso-dodecylphenol, and p-iso-octadecyl-o-tertbutylphenol are used.

In carrying out the reaction of this invention it is important to add the glycidol to

the alkylphenol in order to keep the glycidol from reacting with itself. Therefore, the glycidol is added to the alkylphenol at a rate sufficient to maintain the glycidol concentration in the reaction mass below about 2 per cent, and preferably at about 0.5 per cent or less by weight.

The reaction between glycidol and the alkylphenol is preferably carried out in the presence of a catalytic proportion of an alkaline catalyst. Suitable catalysts include the alkali metals and an oxide, hydroxide, alkoxide, or phenoxide thereof. Typical examples of suitable catalysts include sodium, lithium, potassium, sodium hydroxide, potassium hydroxide, sodium methylate, lithium methylate, sodium isopropylate, sodium octadecylate, sodium phenolate, potassium phenolate, and sodium cresylate. The catalytic proportion of catalyst is generally between about 0.1 and about 2 per cent by weight of the reaction mixture but greater or lesser quantities may be used if desired.

The reaction is carried out at a temperature in the range between about 100 and about 200°C., and preferably in the range between about 130 and about 160°C.

The time required to complete the reaction will vary with the properties of the reactants, the proportions employed, and the degree of polymerization desired. To illustrate a typical reaction, between about 3 and about 6 hours are required to add to the reactor a total of 6 moles of glycidol per mole of isononylphenol in order to yield a product of Formula I in which  $x=5$ . Other time periods can be employed for different alkylphenols or other reaction conditions.

Compounds of the present invention have been found to be not only compatible with concentrated aqueous brine and with concentrated solutions of the hydroxides, phosphates, sulphates, carbonates and silicates of sodium and potassium, but also extremely effective in lowering the surface tensions of such solutions. In contrast, conventional surfactants have not been effective in concentrated aqueous solutions of sodium compounds. The said compounds of this invention are therefore particularly suitable for use as introfiers and wetting-out agents in the kierboiling of raw cotton with alkali, as well as in the mercerization of cotton with caustic soda and in the alkaline pulping of wood for paper. They are also extremely effective in lowering the interfacial tension between oil and water and are excellent for emulsifying concentrated brine solutions with oil. They are also useful as detergents, as additives in dyeing processes, and as dispersants for sulfur, carbon black, pigments, clays and other solids in slurries thereof.

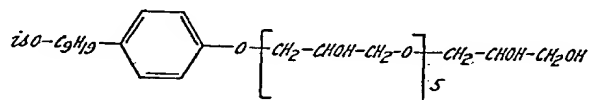
All parts and percentages in the following Examples are by weight unless otherwise specified.

#### EXAMPLE I

The reaction was conducted in a glass-lined vessel fitted with a rapid agitator and reflux condenser. During the heating, a nitrogen atmosphere was maintained in the vessel to prevent discoloration by air.

A mixture of 220 g. technical grade para-isononylphenol (1 mole) and 1 g. of potassium hydroxide was stirred and heated under a blanket of nitrogen at 150°C. and maintained at that temperature ( $\pm 5^\circ\text{C}$ .) while pure, dry glycidol was dripped in gradually at such a rate that the glycidol concentration in the mixture was maintained below about 0.5%. The initial feed rate of glycidol to the glass-lined 3 gallon vessel was in the range between about 3.5 to 5.0 g./min./220 g. para-isononylphenol. The rate of reaction was such that about 4.5 hours was required to add a total of 6 moles of glycidol/mole of isononylphenol to give a product where the value of "x" was 5 in Formula I. During the course of the reaction additional KOH was added when the total alkalinity in the mixture dropped to below 25% of the original value. When this occurred, an additional 0.75 g. KOH was added for each 220 g. of isononylphenol. At the end of the reaction, a quantity of water equal to the weight of the KOH employed was added. Carbon dioxide gas was introduced until the mixture (after cooling the batch to 100°C.) was below pH 9.

Upon cooling to room temperature a viscous amber-colored water-soluble syrup was obtained, the main component of which had the formula:



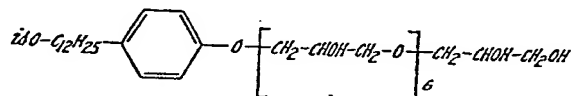
The cloud point of a 1% aqueous solution of this compound was above 100°C.

The para-isononylphenol employed was a technical mixture of isomeric nonyl-phenols obtained by condensing phenol with tripropylene in the presence of acidic catalysts (BF<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>).

It is important in order to obtain high cloud points and compatibility with alkali metal salts that the glycidol reacts with the alkylphenol instead of with itself. This is accomplished as shown in this example by keeping the concentration of free glycidol at a low value at any given moment.

#### EXAMPLE II

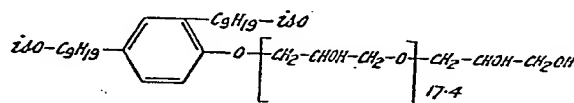
In the same manner as described in Example I, paraisododecylphenol (made from phenol, tetrapropylene and BF<sub>3</sub>) was reacted at 150°C. with glycidol, using 88.5 g. para-iso-dodecylphenol, 0.24 g. potassium metal, and 173 g. glycidol which was added with agitation over a 3 hour period. The product was a very viscous semi-solid water-soluble material the main component of which had the formula:



The cloud point of a 1% aqueous solution of this compound was greater than 100°C.

#### EXAMPLE III

In the same manner as described in Examples I and II, o-p-di-isononylphenol (1 mole) was reacted with 18.4 moles of glycidol at 150°C. in the presence of metallic potassium (0.3% by weight of the di-isononylphenol) with agitation over a 5 hour addition period. The product was a viscous, semi-solid, water-soluble material the main component of which had the formula:

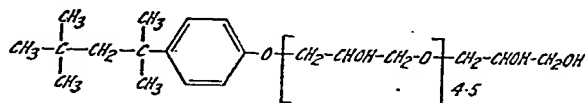


The cloud point of a 1% aqueous solution of this compound was above 100°C. The di-isononylphenol used was made from phenol and tri-propylene with BF<sub>3</sub> catalyst and was the technical commercially available product.

#### EXAMPLE IV

In the same manner as shown in Example II, one mole of para-tertiary-octylphenol (made from phenol, diisobutylene and BF<sub>3</sub>) was reacted in the presence of 0.4% by weight of metallic sodium at 140°C. with 5.5 moles of glycidol which was added over a four hour period with agitation.

The product was viscous water-soluble syrup the main component of which had the formula:



The cloud point of a 1% aqueous solution of this compound was above 100°C. Although it is known in the prior art (U.S. Patent No. 2,089,569) that phenol, cresol, xylenol, naphthol, and various alcohols, amines, and carboxylic acids can be reacted with glycidol to give addition products, it has not been possible until the present invention to obtain surface-active compounds having the unique combination of properties described herein; namely, cloud points over 100°C. and complete compatibility with concentrated or saturated aqueous solutions of alkali metal chlorides, hydroxides, carbonates, sulphates, phosphates, and silicates.

The following table lists the properties of these new materials compared to similar non-ionic surfactants based upon ethylene oxide,

I — Cloud Point °C., 1g. Surfactant per 100 ml. Solution

A — Novel Surfactant, Adduct of Glycidol and p-isononylphenol

Moles Glycidol	Distilled Water	NaCl 25% soln	Na <sub>2</sub> CO <sub>3</sub> 15% soln.	Na <sub>2</sub> SiO <sub>3</sub> 10% soln.	NaOH 20% soln.	Na <sub>2</sub> SO <sub>4</sub> 10% soln.	Na <sub>3</sub> PO <sub>4</sub> 9% soln.
10	>100°C.	>100°C.	>100°C.	>100°C.	>100°C.	>100°C.	>100°C.
8.9	"	"	"	"	"	"	"
8.0	"	"	"	"	"	"	"
7.0	"	"	"	"	"	"	"
6.0	"	41°C.	10°C.	55°C.	86°C.	22°C.	34°C.

B — Known Surfactant, Adduct of Ethylene Oxide and p-isononylphenol

Moles Ethylene Oxide							
30	>100°C.	43°C.	<0°C.	<0°C.	<0°C.	17°C.	46°C.
15	"	38°C.	"	"	"	25°C.	48°C.
10.5	71°C.	17°C.	"	"	"	7°C.	31°C.
9.0	56°C.	4°C.	"	"	"	<0°C.	18°C.

It can be seen from the table that p-isononylphenolglycidol adducts possess greater compatibility and solubility than do the ethylene oxide adducts; and this in general also holds for the other homologous alkylphenol-glycidol adducts as described herein.

#### EXAMPLE V

Novel adducts of this invention were prepared in accordance with a procedure similar to Example I from nonyl phenol and glycidol in various proportions. The resulting adducts were subjected to the Draves wetting test, in which the time for a standard skein of cotton to sink in a cylinder of a solution of the adduct at 60°C. is measured. Results of these tests are as follows:

Draves Wetting Time, Seconds at 60°C., Distilled Water

Composition	Concentration	
	0.1%	0.25%
Nonyl phenol + 10 moles glycidol	15.0 sec.	5.6 sec.
„ „ 8.9 „ „	16.1 sec.	5.6 sec.
„ „ 8 „ „	13.8 sec.	3.5 sec.
„ „ 7 „ „	11.0 sec.	3.7 sec.
„ „ 6 „ „	9.0 sec.	2.2 sec.

#### EXAMPLE VI

A novel adduct was prepared in accordance with a procedure similar to that of Example I from nonyl phenol and 8.9 moles of glycidol.

Various proportions of the adduct were added to various aqueous brine solutions and the force required to pull a loop of platinum wire from the surface was measured to obtain the surface tension. Corresponding solutions were covered with mineral oil and the force required to pull a loop of platinum wire through the interface was measured to determine the interfacial tension. Results of these measurements were as follows:

Surface and Interfacial Tensions in NaCl Solutions Surfactant —  
Nonyl phenol and 8.9 moles glycidol

Medium	Surfactant Concentration %	Surface Tension	Interfacial Tension
25% NaCl	0	79.5	54.5
"	0.0063	31.9	2.8
"	0.0097	31.3	2.5
"	0.0280	29.9	1.8
"	0.0494	29.9	1.6
"	0.0794	30.4	1.5
"	0.1702	29.9	1.5
20% NaCl	0.001	35.3	6.1
15% NaCl	0.001	35.8	7.7
10% NaCl	0.001	37.2	9.4
5% NaCl	0.001	44.0	13.5
Distilled Water	0.001	45.7	17.7

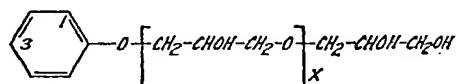
These measurements show that the surface tension and interfacial tension of concentrated brines are lowered substantially by the novel adduct of this invention. In addition, the novel surfactant is more effective in brine than in distilled water.

#### EXAMPLE VII

To illustrate the emulsifying properties of the novel adducts, three grams of the six mole glycidyl ether of nonyl phenol was dissolved or dispersed in 97 grams of orthodichlorobenzene. Five milliliters of the resulting solution or dispersion was added to 95 milliliters of water and shaken slightly. A "flash" emulsion formed, which was stable overnight.

For purposes of comparison, the procedure was repeated employing the 9 and 10.5 mole ethylene oxide adducts of nonyl phenol. In each instance, the emulsions were poor and separation of phases was noted within minutes.

1. A process for preparing a water-soluble adduct of glycidol and an alkylphenol, said adduct having the formula



in which one of the numbered positions in the benzene ring is occupied by an alkyl group having 8 to 18 carbon atoms, and the other numbered position is occupied by hydrogen or an alkyl group having 1 to 18 carbon atoms, wherein x has a value of at least 4.5, and wherein the ratio of the value of x to the total number of carbon atoms in the alkyl groups at positions No. 1 and No. 3 is at least 0.50, which process comprises adding glycidol to an alkylphenol heated to a temperature in the range between 100 and 200°C. at a rate sufficient to maintain the glycidol concentration in the resulting reac-

tion mass below about 2% by weight for a sufficient time to yield a product in which x in the above formula is above at least 4.5.

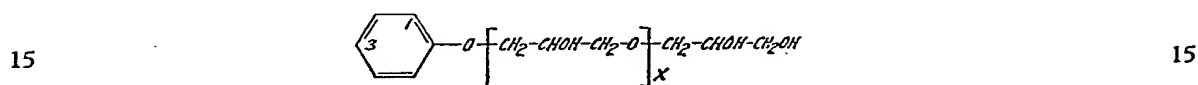
2. A process according to Claim 1, wherein a catalytic proportion of an alkali metal catalyst is added to the alkylphenol prior to the addition of glycidol.

5 3. A process according to Claims 1 or 2, wherein between about 3 and about 6 hours are required to add glycidol in a proportion equivalent to 6 moles of glycidol per mole of alkylphenol present. 5

4. A process according to any one of Claims 1—3, wherein the reaction is maintained within the range between about 130 and about 160°C.

10 5. A process according to any one of claims 1—4, wherein the alkylphenol is p-isononylphenol, p-isododecylphenol, o-, p-di-isononylphenol, p-tertiary-octylphenol, or o-p-di-tertiary-octylphenol. 10

6. A water-soluble adduct of glycidol and an alkylphenol, said adduct having the formula



in which one of the numbered positions in the benzene ring is occupied by an alkyl group having 8 to 18 carbon atoms, and the other numbered position is occupied by hydrogen or an alkyl group having 1 to 18 carbon atoms; wherein x has a value of at least 4.5, and wherein the ratio of the value of x to the total number of carbon atoms in the alkyl group at positions No. 1 and No. 3 is at least 0.50.

20 7. An adduct according to Claim 6, wherein the alkylphenol is p-isononylphenol, p-isododecylphenol, o-, p-di-isononylphenol, p-tertiary-octylphenol, or o-p-di-tertiary-octylphenol. 20

8. A process for preparing a water-soluble adduct of glycidol and an alkylphenol, substantially as hereinbefore described in any one of the Examples I to VI. 25

9. An adduct, whenever prepared according to the process claimed in any one of Claims 1 to 5 or 8.

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